

Vaporization Studies of Olivine via Knudsen Effusion Mass Spectrometry

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Introduction

Olivine is the major mineral in the Earth's upper mantle occurring predominantly in igneous rocks and has been identified in meteorites, asteroids, the Moon and Mars. Among many other important applications in planetary and materials sciences, the thermodynamic properties of vapor species from olivine are crucial as input parameters in computational modelling of the atmospheres of hot, rocky exoplanets (lava planets).¹ There are several weight loss studies of olivine vaporization in the literature²⁻⁴ and one Knudsen Effusion Mass Spectrometry (KEMS) study⁵. In this study, we examine a forsterite-rich olivine (93% forsterite and 7% fayalite, $\text{Fo}_{93}\text{Fa}_7$) with KEMS to further understand its vaporization and thermodynamic properties.

Experimental: Starting Material and Characterization

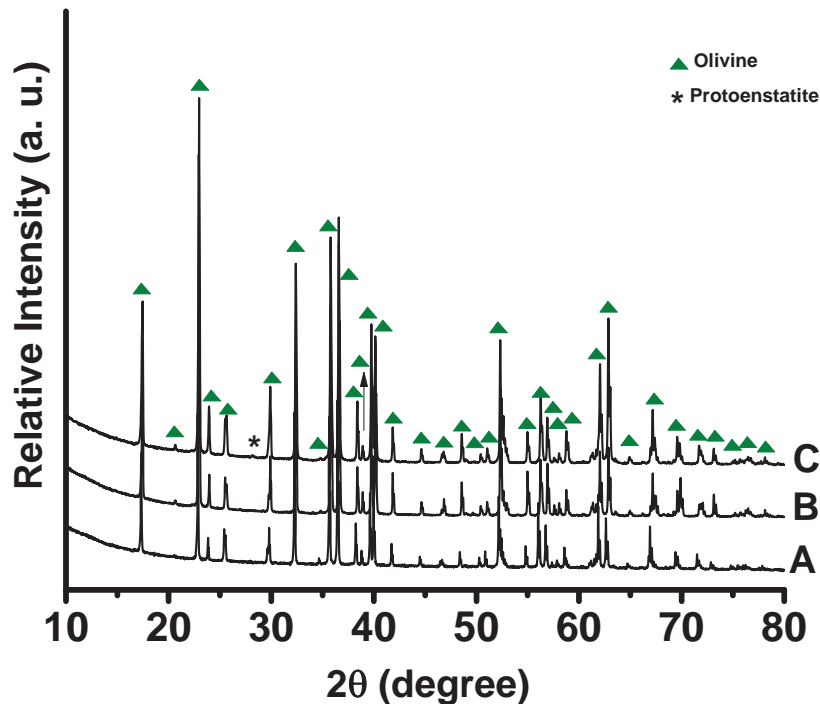
Sample studied in this scientific work was mined from the west coast of Norway by Nor Mineral and provided by Miller & Co., Chicago, IL. The phase evolution and composition of the samples before and after KEMS experiments were characterized using X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES) and electron microprobe analysis. An analysis of the starting material is given below. In our preliminary studies, the identification and volatility sequence of the of the vapor species as well their vaporization coefficients and the melting point of olivine were derived from KEMS.

Element	*Wt (%)
Al	0.0120(6)
Ca	0.035(2)
Co	0.0120(6)
Cr	0.052(3)
Fe	5.01(3)
Mg	30(2)
Mn	0.075(4)
Na	0.0080(4)
Ni	0.27(1)
Sc	0.0040(2)
Si	20(1)

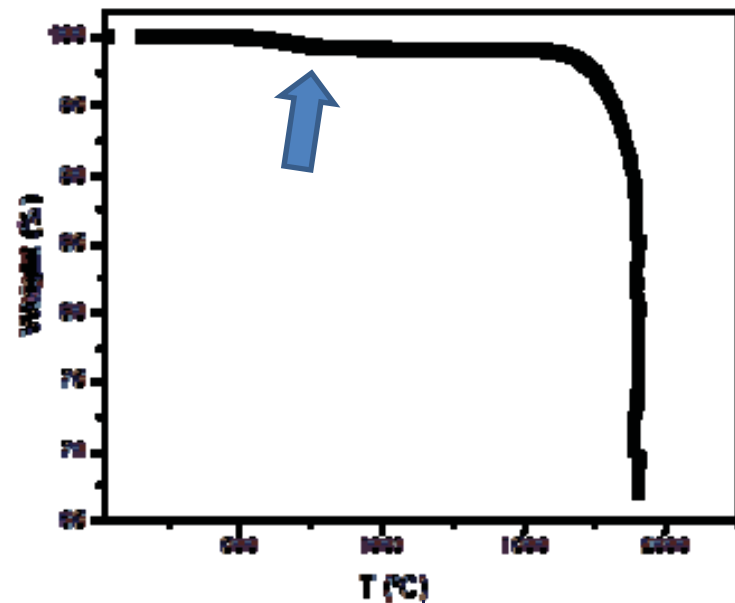
*Uncertainties of the analyses are given in parentheses

Experimental: Impurities in Starting Material

We found the initial material gave inconsistent KEMS signals. This was attributed to impurities, chiefly clinochlore $(\text{Mg, Fe, Al})_6(\text{Si, Cr})_4\text{O}_{10}(\text{OH})_8$. We found that a heat treatment $> 1060^\circ\text{C}$ removed this secondary phase. This is evident in the thermogravimetric (TGA) trace below, which shows a weight loss starting at about 900°C . The XRD pattern of the post-heat treated olivine was similar to that of a purified green sand sample from Hawaii, which is a Fo-rich form of olivine.

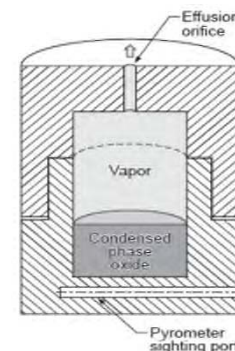
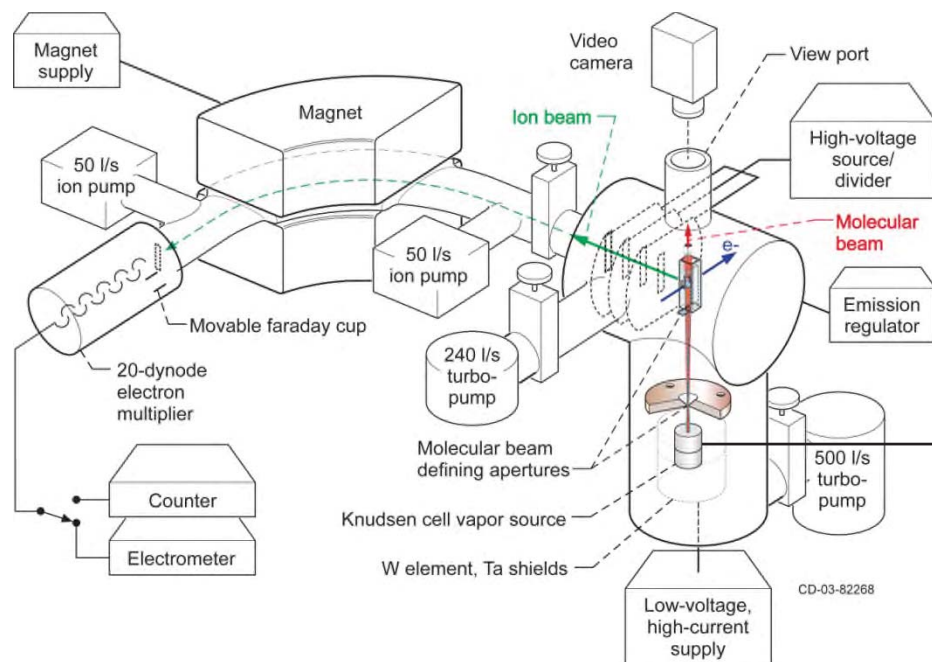


XRD patterns of the olivine samples : (A) green sand from Hawaii, (B) after KEMS up to 1850 K in a Mo Knudsen cell (C) after KEMS up to 2079 K in an Ir Knudsen cell.



Thermogravimetry (TG) traces on heating of the olivine sample.

Experimental: Knudsen Effusion Mass Spectrometry (KEMS)



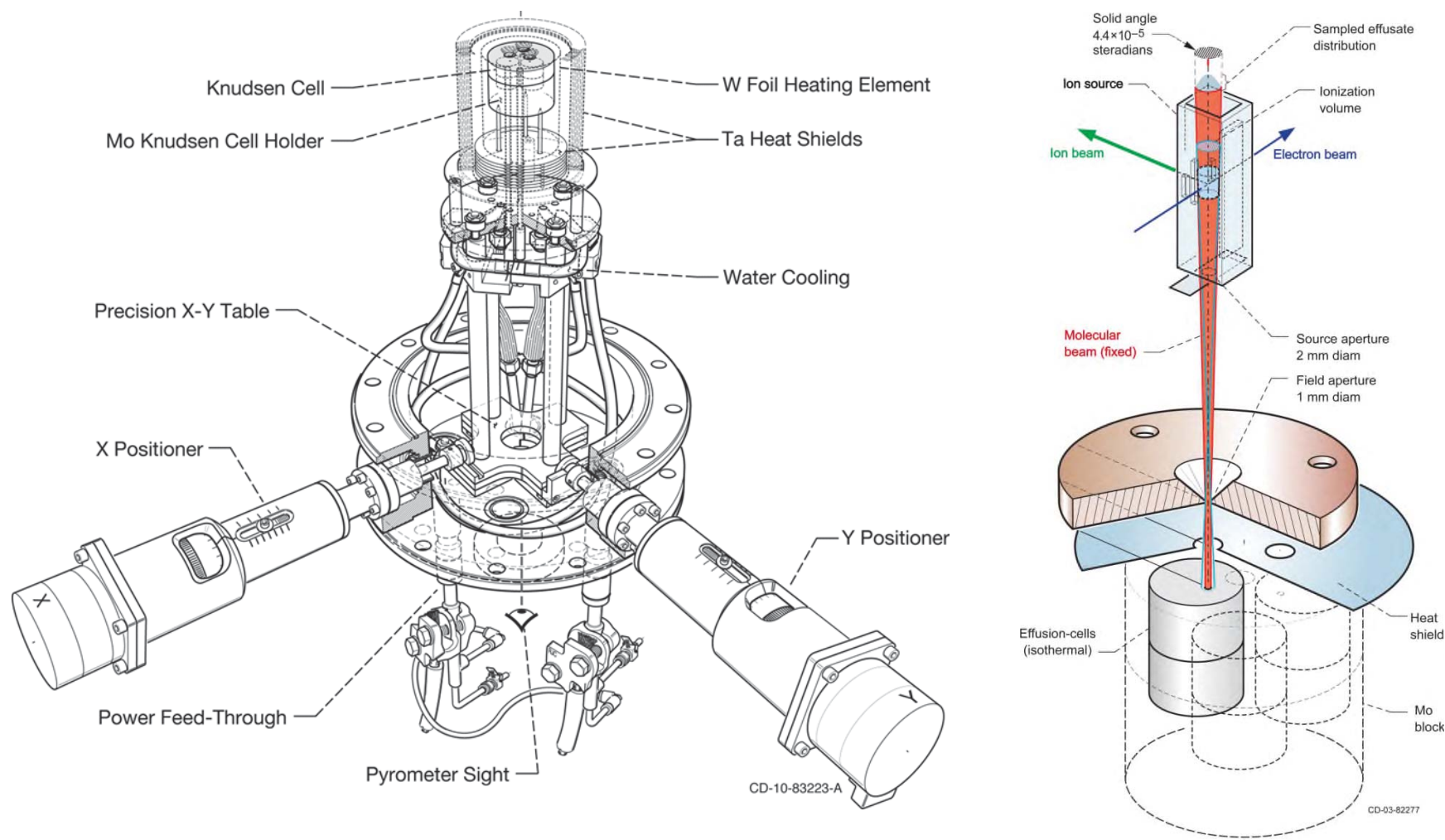
The partial pressures of the species inside of the effusion-cell is proportional to the ion intensity according to the relationship: $P = \frac{kIT}{\sigma}$

P - partial pressure of the species,
 k - instrument constant,
 I - measured ion intensity of the species,
 σ - ionization cross section^{6,7}.

The vapor composition and partial pressure of the vapor species were measured in a Nuclide/MAAS/PATCO 12-90-HT single-focus 90° magnetic-sector mass spectrometer. This instrument has the following features:

- Resistance heating of cells to 2000°C
- Molecular beam/ionizing electrons/ion beam mutually perpendicular
- Non-magnetic source, magnetic analyzer, detection via ion counting \Rightarrow no dependence of ion intensity on mass number
- Temperature calibration from melting point of Au (ITS-90 standard)
- System optimized for thermodynamic measurements of inorganic compounds

Unique Sampling Arrangement: Restricted Collimation^{7,8}



The Field aperture is smaller than the cell orifice and ionizer effectively ‘sees’ only inside the cell.

- Reduces background
- Measuring only intrinsic properties of compound in cell

Method of Measuring Vaporization Coefficients^{9,10}

The Multiple-cell configuration with Knudsen cells with different orifice diameters and restricted collimation was used to obtain the vaporization coefficients, α , of the vapor species. Whitman-Motzfeld method was used to calculate the vaporization coefficients, α :

$$P_m = P_{eq} - P_m f \left(\frac{1}{\alpha} + \frac{1}{W_A} - 2 \right) \quad f = \frac{W_B B}{A}$$

P_m - measured vapor pressure,

P_e - equilibrium vapor pressure,

α - vaporization coefficient (“barriers to vaporization”),

W_A - transmission factor of the cell body,

W_B - transmission factor of the orifice.

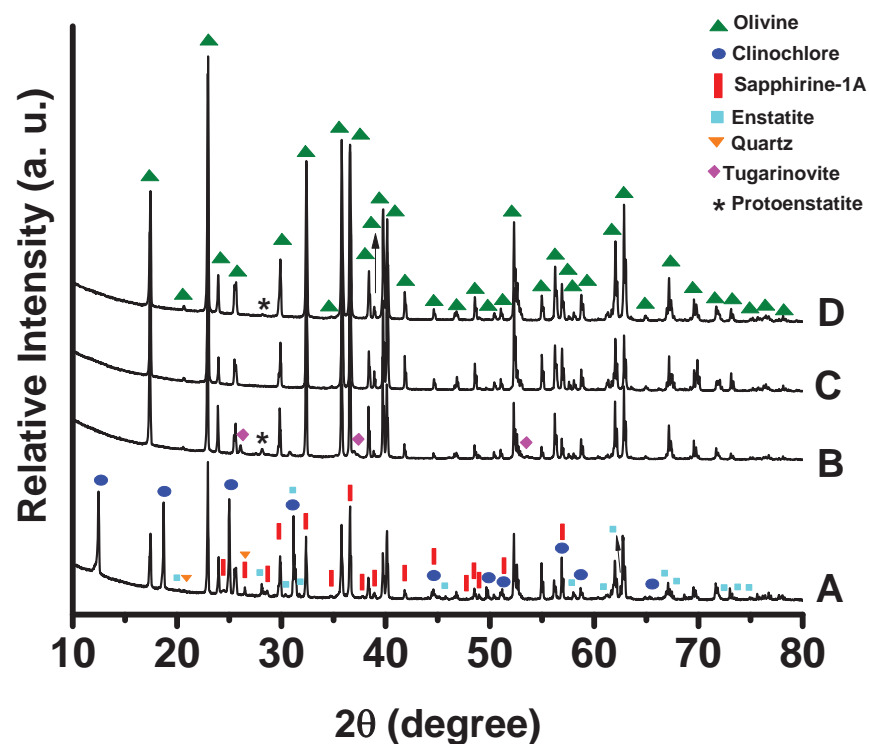
A - cross sectional area of the cell,

B - cross sectional area of the orifice.

This equation combined with the relationship of partial pressure to ion intensity of cells with different orifice geometries (designated 1, 2):

$$\alpha = \frac{f_2 - f_1 \left(\frac{p_1}{p_2} \right)}{\left(\frac{p_2}{p_1} \right) - 1} = \frac{f_2 - f_1 \left(\frac{I_1}{I_2} \right)}{\left(\frac{I_2}{I_1} \right) - 1}$$

Results: XRD and Crucible Selection



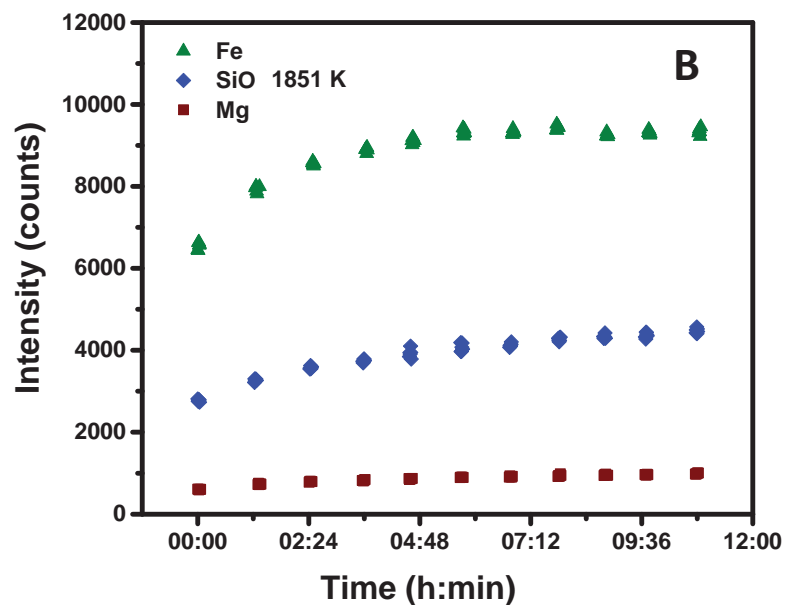
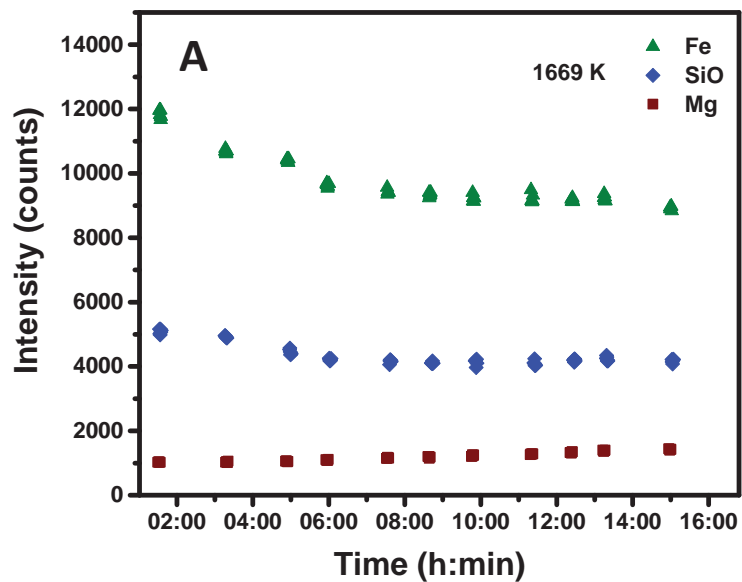
XRD patterns of the olivine samples : (A) as received , (B) after KEMS up to 2084 K in a Mo Knudsen cell (C) after KEMS up to 1850 K in a Mo Knudsen cell (D) after KEMS up to 2079 K in an Ir Knudsen cell.

Crucible selection is a challenge for reactive silicates such as olivine. We have initially tried Mo cells due to their lower cost and machinability, but have found these form Mo compounds with the olivine and give erratic signals in the KEMS, particularly above the melting point. However, Ir cell liners in a graphite cell have proved unreactive.



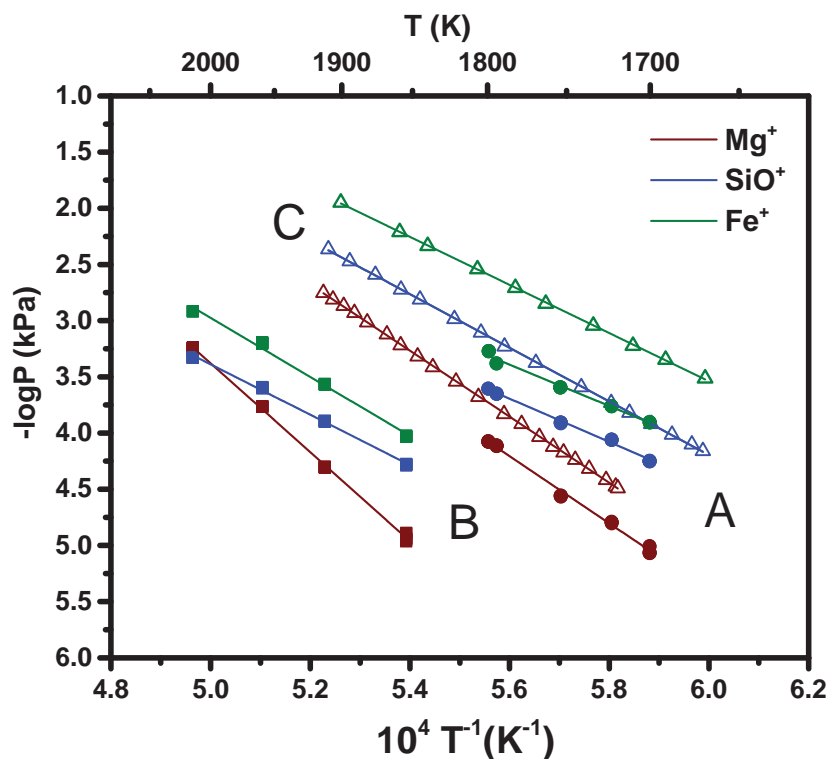
Side view (cross-section) of the Mo Knudsen cell containing the olivine sample heat treated up to 2084 K.

Results: Time to Equilibration



KEMS equilibrium studies can only be conducted after the ion intensities are constant with time. These figures show the principle vapor species and the time to reach a constant value. **(A)** in a molybdenum Knudsen cell and **(B)** in an iridium Knudsen cell.

Results: van't Hoff Plot



van't Hoff plot of the main species vaporized from the olivine samples: (closed squares, **A**) this study using an Ir Knudsen cell, (closed circles, **B**) this study using a Mo Knudsen cell and (opened triangles, **C**) using a Re Knudsen cell, Piacente et al.⁵

Clausius-Clapeyron equations of the species vaporized from the olivine samples.

(A) This study - Ir Knudsen cell

$$\log P_{Mg} (KPa) = 16.40 \pm 0.15 - 39.57 \pm 0.03 \cdot 10^3 T^{-1}$$

$$\log P_{SiO} (KPa) = 7.83 \pm 0.13 - 22.43 \pm 0.02 \cdot 10^3 T^{-1}$$

$$\log P_{Fe} (KPa) = 10.16 \pm 0.23 - 26.27 \pm 0.04 \cdot 10^3 T^{-1}$$

(B) This study - Mo Knudsen cell

$$\log P_{Mg} (KPa) = 12.53 \pm 0.22 - 29.88 \pm 0.04 \cdot 10^3 T^{-1}$$

$$\log P_{SiO} (KPa) = 7.08 \pm 0.14 - 19.24 \pm 0.03 \cdot 10^3 T^{-1}$$

$$\log P_{Fe} (KPa) = 6.91 \pm 0.22 - 18.40 \pm 0.03 \cdot 10^3 T^{-1}$$

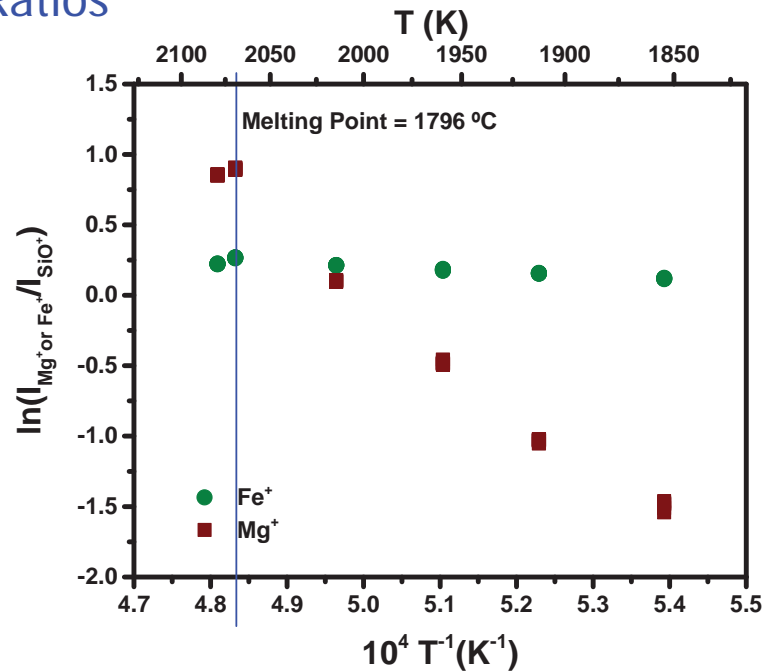
(C) Re Knudsen cell, Piacente et al.⁵

$$\log P_{Mg} (KPa) = 12.18 \pm 0.68 - 28.6 \pm 0.7 \cdot 10^3 T^{-1}$$

$$\log P_{SiO} (KPa) = 10.21 \pm 0.36 - 24.0 \pm 0.8 \cdot 10^3 T^{-1}$$

$$\log P_{Fe} (KPa) = 9.34 \pm 0.72 - 21.4 \pm 0.8 \cdot 10^3 T^{-1}$$

Results: Determine Melting with Ion Intensity Ratios



Temperature dependence of ion intensity ratios of Mg⁺, Fe⁺ and SiO⁺ in the olivine sample.

The ion intensity ratios of the Mg-Fe-SiO system are proportional to their partial molar Gibbs energies of vaporization and are linear with T^{-1} in a solid or liquid region. When a phase change occurs a change in slope is expected.^{12,13}

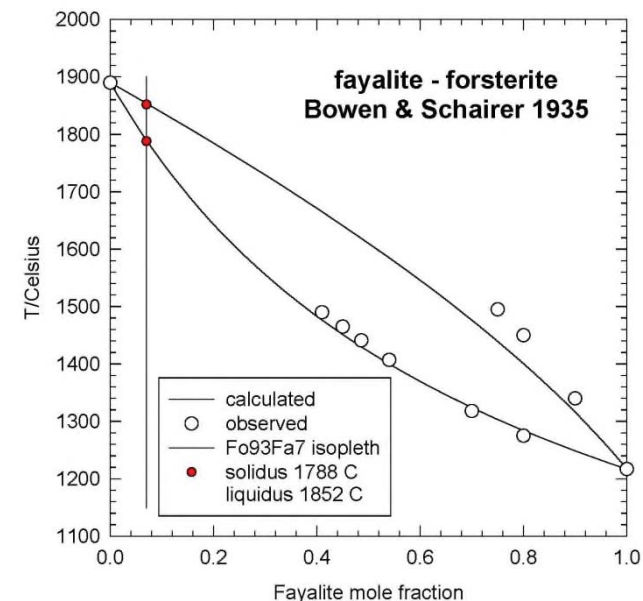
$$\ln(I_A/I_B) = \frac{\Delta_{\text{vap}}\bar{G}_B^i - \Delta_{\text{vap}}\bar{G}_A^i}{RT} + \tilde{C}$$

$\Delta_{\text{vap}}\bar{G}$ - partial molar Gibbs energies of the species,

\tilde{C} - instrument constant,

R - gas constant,

T - temperature.

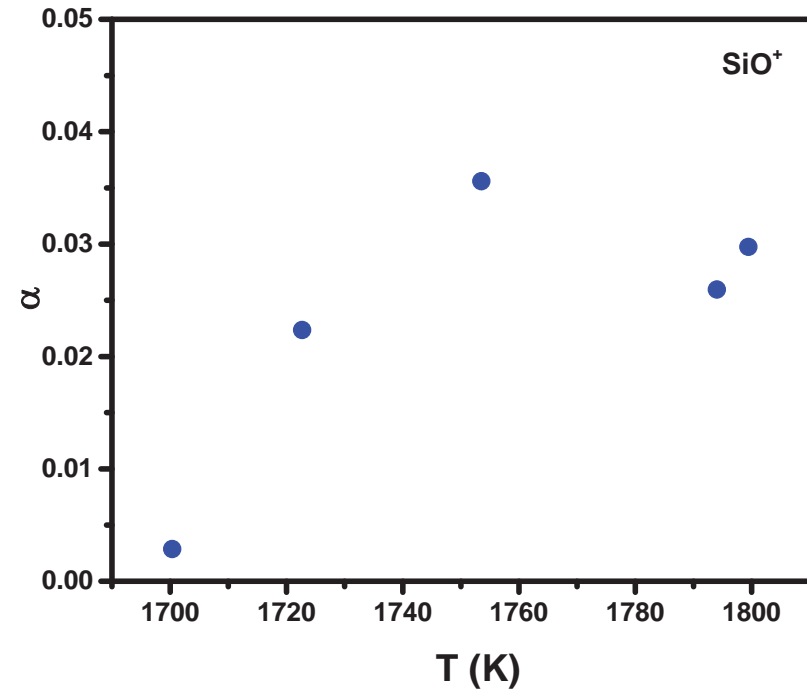
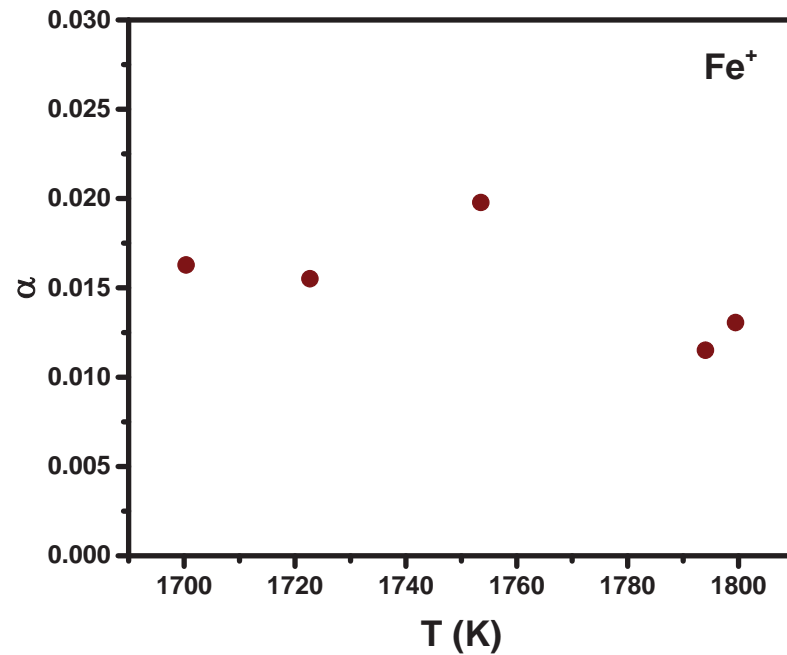


Fegley and Osborne, "Practical Chemical Thermodynamics For Geoscientists, Elsevier 2013, Fig. 12-11.

Measurements show good agreement with the phase diagram calculated by Bowen and Shairer¹⁴.

Vaporization coefficients

- Kinetic factors that lower observed vapor pressures;
- Influence the vaporization/fractionation of silicate melts;
- Useful in diverse fields e.g. condensation cloud formation/evaporation in atmospheres of brown dwarfs and exoplanets, oxide deposition, and slag chemistry.



Measured Vaporization coefficients of Fe^+ and SiO^+ using three Mo Knudsen cells with different orifice sizes.

Summary

- Secondary phases of the olivine sample were removed at temperatures $> 1060\text{ }^{\circ}\text{C}$.
- Mo cell reacts with olivine sample. Ir must be used
- The main vapor species of the olivine sample are Mg^+ , SiO^+ and Fe^+ following this order of evaporation.
- The melting point of the olivine sample was determined by the ion intensity ratio method to be $1796\text{ }^{\circ}\text{C}$.
- Vaporization coefficients and temperature dependence of partial pressures of the species were determined.

Acknowledgements

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